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The determination of
ammonia nitrogen in water

Chemical Engineering

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THE DETERMINATION OF AMMONIA
NITROGEN IN WATER

BY

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THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

IN CHEMICAL ENGINEERING

IN THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Benjamin Harrison Harrison

ENTITLED The Determination of Ammonia Nitrogen in Water

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Chemical Engineering

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HISTORICAL.

Wanklyn Chapman and Smith* in eighteen hundred and sixty

*Journal Chemical Society, 1867, p. 445.

seven, were the first to introduce methods for the determination of nitrogen in water. In their first paper, the authors proposed to divide the distillation into three parts. First the water should be distilled with the addition of sodium carbonate, secondly with caustic potash and thirdly with potassium permanganate. The ammonia in the distillates was to be determined colorimetrically by comparing with standards by the use of Nessler reagent. The first distillate was supposed to contain the ammonia that was originally present in the water as such or as ammonium salts, plus that derived from the destruction of urea and allied substances; the second distillate about one-third of the ammonia corresponding to the nitrogen of albumen, gelatin, etc.; and the third distillate the remaining two-thirds of the ammonia of these substances.

In the following year, Wanklyn* gave the results of some

*Journal Chemical Society, 1867, p. 591.

experiments made to prove the correctness of his method. In this series the second and third distillations were united, that is, the caustic potash and potassium permanganate were added at the same time. He discovered that the process as thus carried out did not yield ammonia corresponding to the total amount of nitrogen present, but two-thirds or at any rate a constant fraction of

the total amount. If the boiling was carried to dryness, however, the total nitrogen was obtained as ammonia. To the ammonia obtained on the addition of sodium carbonate he gave the name of free or saline ammonia and to that obtained on the addition of the caustic potash and permanganate the name albuminoid ammonia.

In the following year, the three original authors*

*Journal Chemical Society, 1868, p. 152.

published a paper, mainly devoted to a criticism of Frankland and Armstrong's* combustion process. They gave results derived from

*Journal Chemical Society, 1868, p. 77.

various quantities of water experimented on. They placed reliance on the constancy of the ratio of the amount of nitrogen found to the amount of water taken. Thus if they took one-half liter of water for the determination the amount of nitrogen found was one-half that obtained if one liter of the same was distilled or the amount of nitrogen found was proportional to the quantity of water taken.

In May of the same year Wanklyn and Chapman* published

*Journal Chemical Society, 1868, p. 161.

results showing the nitrogen obtained from definite substances, in which they used amines, amides and natural alkaloids. They drew the conclusion that the action of the alkaline permanganate was in each case perfectly definite. In various cases yielding one-third, two-thirds, all or none of the organic nitrogen

according to the substance in question.

The ease of manipulation and its simplicity quickly brought the method into common use until now it is probably more used for the determination of ammonia in water than any other method. It has been criticized from the start for various reasons and by various authors.

Frankland and Armstrong* hold that it did not afford a

*Journal Chemical Society, 1868, p.97.

measure of the organic matter present, neither the whole amount nor a constant fraction of it being evolved as ammonia according to experiments by themselves. They hold that the albuminoid ammonia process could not be used to indicate either the presence or the proportion of albuminoid as distinguished from other forms of nitrogenous organic compounds. Peaty waters in which it is assumed that albuminoid compounds cannot be present yielding a large proportion of its nitrogen as so-called albuminoid ammonia. They come to the conclusion that the process is entirely useless in the examination of waters for sanitary purposes.

Miller*says, "it is simple and elegant, and will probably

*Journal Chemical Society 1878, p. 58.

form a leading feature in our future methods for it admits of graduation and may serve to distinguish one impurity from another. Unfortunately, however, it deals with bodies at present unknown, in a manner in which we are ignorant; its results, therefore, admit of no precise interpretation and can aid only in distinguishing a

bad water from a good one."

Tidy* thinks the importance of the objection based on the

*Journal Chemical Society, 1879, p. 59.

variable yields of nitrogen as ammonia by different substances is overrated; as the main question is whether, on the whole, the yield of ammonia keeps pace with the purity or impurity of the water examined. He then presents some other objections.

1. He believes that it is practically impossible to prepare an alkaline permanganate solution free from ammonia.

2. He considers it extremely difficult to exhaust the action of alkaline permanganate finding that if distillation is carried until no more ammonia is evolved and then the apparatus set aside, more ammonia is evolved, at times an amount greater than that obtained in the first case.

3. He has on various occasions noticed the disappearance of ammonia. The total ammonia being less than the blank which was run.

4. He doubts whether tint in a solution can be made the basis of accurate quantitative measurements, but that there is an error varying with different eyes, and as three or four tubes are read in one determination this error will be multiplied by three or four. He also thinks that since we only distill 500 c.c. of water and calculate to parts per million, or grams per 1000 c.c. that we are multiplying any error in our result by two.

Mallet* says of this objection, "The estimation of

*Report National Board of Health, 1882.

ammonia by means of Nessler reagent involves not an accurate judgment of depth of tint of a single liquid, but a comparison of such tint when produced by a standard solution of ammonia of known strength. The two liquids of the same character being seen by the same eyes at the same time, the error referred to can only consist in a lack of sensitiveness on the part of the observer for small differences in depth of tint. There is no reason that the direction of this error should be constantly or more frequently on one side of the truth than the other; hence the consequence of three or four estimations being made instead of one is a probability that the error to the final result will be less instead of greater than the error of a single observation, and surely there is no change produced in the ratio of the error to the whole quantity determined by representing the latter on the basis of parts in a million rather than parts in five hundred thousand. An error of .01 on .25 parts of ammonia in 500,000 represents exactly the same degree of accuracy as an error of .02 on .50 in 1,000,000."

The extensive use of the albuminoid process shows that it has many followers, and the results of long usage, while there are occasional objections or conditions under which it cannot be used, show that it has a value in determining the purity of a water. It is not the purpose of this thesis to confirm the results of certain experimenters who have worked on this subject, for some of the experiments have been carried out on a scale far greater than could be done in a work of this nature, but to consider the method from a little different standpoint, namely,

the interference of various salts and compounds ordinarily found in waters.

In general we have followed methods which have been tested by various investigators and upon which nearly all authorities agree. Some of the most important are the following:

1. A constant rate of distillation.

Under the best conditions there is apt to be an imperfect condensation of ammonia in distilling, varying from one to twelve per cent of the total amount. It has been pointed out that this loss is proportional to the rate of distillation, i.e. the faster the distillation other things being equal the greater the loss.

2. A uniform temperature for Nesslerization.

The distillates in nesslerizing must be at the same temperature as the standards. Hazen and Clark* have shown that .04

*Am. Chem. Journ. 1890, p. 425.

parts of nitrogen as ammonia at 30°C reads .05 parts at 16°C and .06 parts at 0°C. The best procedures now state that the distillates should be left over night before nesslerizing in order to allow them to come to room temperature.

3. Uniform organic ammonia in comparative tests.

In the case of albuminoid ammonia various nitrogenous substances give up a certain percentage of their nitrogen as ammonia which is constant for a given substance but varies between large limits with different substances, and that there are a great many substances which continue to give off ammonia when the distillation must be stopped on account of the concentration of the solution.

INTRODUCTION.

In our study we have planned to consider the interference by substances that are ordinarily present in natural waters. There are certain ions which are nearly always present, and which may combine with each other in various ways to form different compounds. An analysis of the mineral content of a water, will usually show the presence of the ions Si, Fe, Al, Ca, Mg, Cl, NO₃, SO₄, Na, K, and NH₄, which may combine forming SiO₂, Fe₂O₃, Al₂O₃, CaCO₃, CaSO₄, MgSO₄, MgCO₃, MgCl₂, KCl, NaCl, KNO₃, etc., the compounds formed varying in different waters with the amount of the various ions present. In mineral waters hydrogen sulphide and other gases are sometimes found. It was the purpose of this work to see if the presence of any of these constituents held back any of the ammonia during the distillation or interfered in any way with the determination of nitrogen as ammonia.

The procedure followed in these experiments for the determination of free and albuminoid ammonia was that recommended by the Committee of the American Public Health Association in the report on Standard Methods of Water Analysis.

Former experimenters have found that the use of rubber connections on the apparatus for the distillation of ammonia is a continual source of danger. Some authorities recommend the boiling of all such connections for two days in Nessler reagent and more recently the use of apparatus in which rubber is not used at all as a connection. The apparatus used in this work consisted entirely of glass, and was of the same design as that in use by the Chicago Department of Health. It consisted of a jena glass liter flask A,

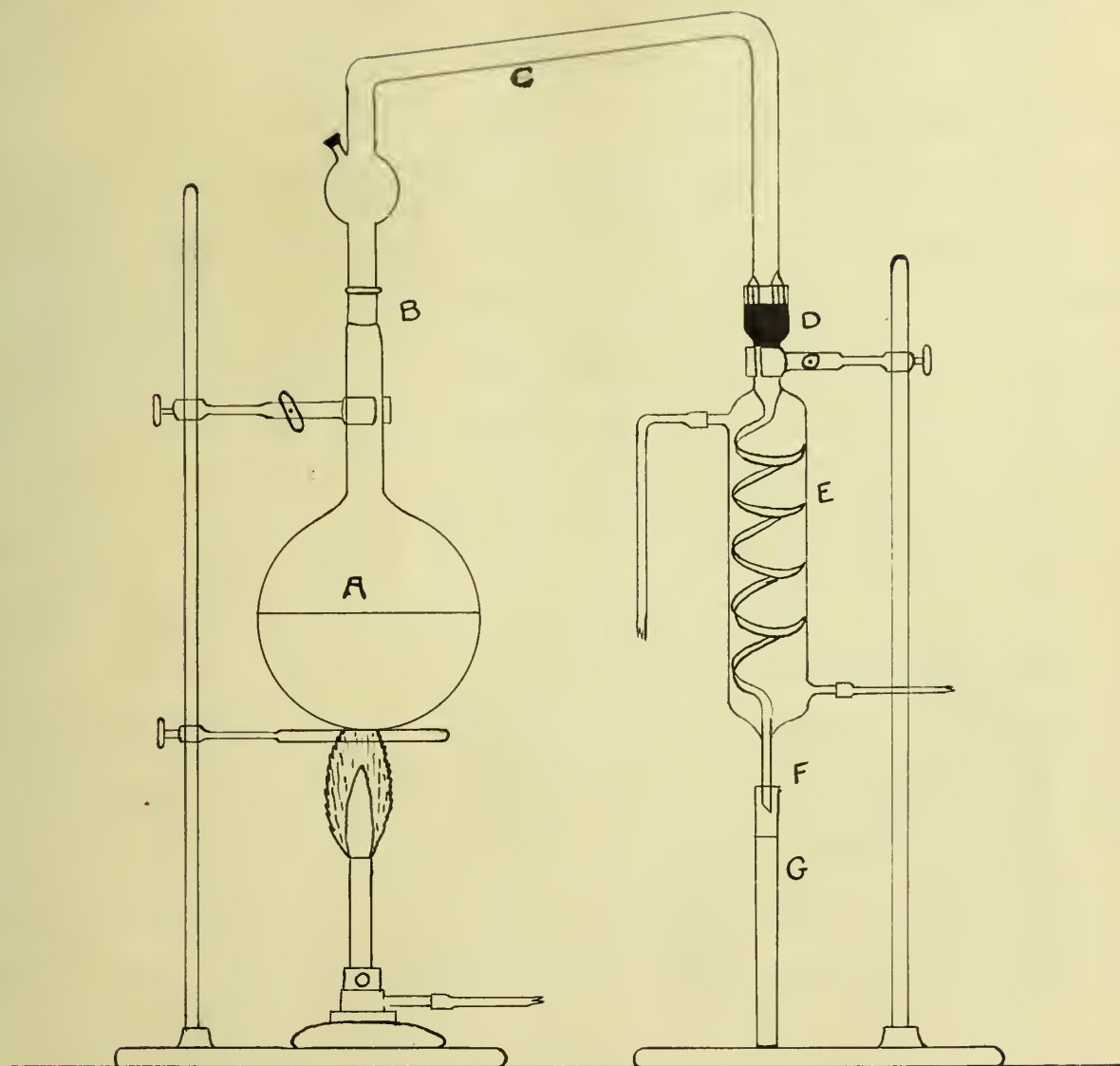


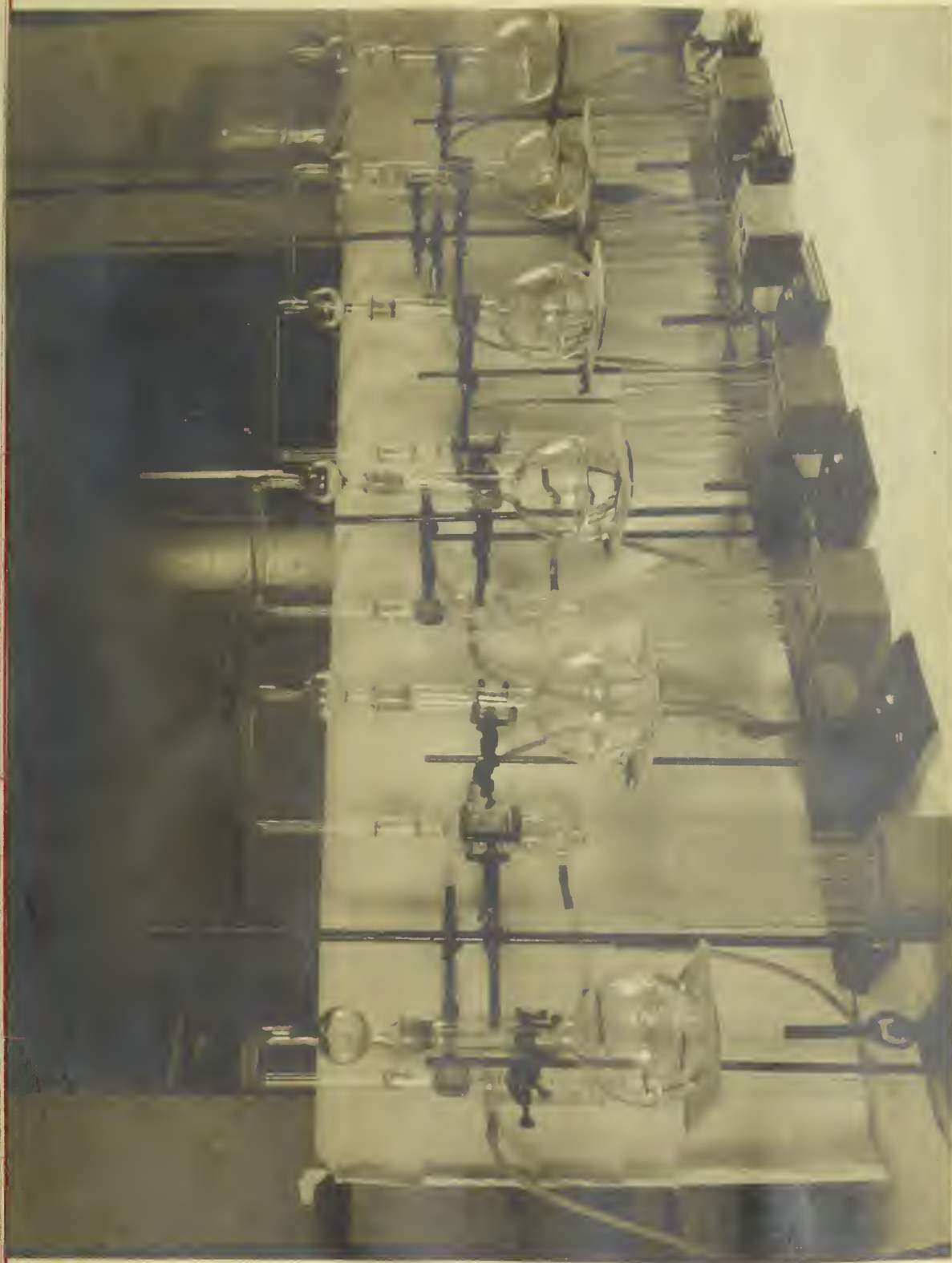
Diagram of Distillation Apparatus

(See Diagram page 7a), the neck of which is ground at B to receive the connecting glass tube C., the other end of which dips into a mercury cup at D connecting the flask with the condenser E. The lower end of the condenser F is narrowed down and dips into the Nessler tube G which is changed when filled to the mark.

In making a determination of ammonia the flask, connecting tube and condenser are cleaned by boiling water in the flask until the distillate shows no further trace of ammonia. The flask is then emptied and 500 c.c. of the water to be examined is measured into it. One gram of sodium carbonate and three tenths of a gram of pumice stone are added and heat is applied so that the distillation will be at the rate of not more than ten or less than six cubic centimeters per minute. Four Nessler tubes of the distillate containing 50 c.c. each are collected and contain the free ammonia.

Fifty cubic centimeters of alkaline permanganate are then added and four more tubes of 50 c.c. each collected. These contain the albuminoid ammonia. To the tubes containing the free and albuminoid ammonia one cubic centimeter of Nessler reagent is added, and after twenty minutes their color is compared with standards which contain known amounts of ammonium chloride treated in the same way at the same time.

The minute quantities of ammonia in water requires the utmost care in the preparation and handling of reagents to keep them from being contaminated. Unless extreme care is taken at all times, the amount of ammonia which will get in as contamination may be as great as that present in the original sample. In this connection it might be well to cite an example that happened in the early stages



View of Apparatus for Ammonia Distillations

of this experiment.

PRELIMINARY TESTS.

The Division of Physiological Chemistry was keeping two dogs and a wolf for experimental purposes in a room near where this work was being done and at times there was a strong odor coming from this room. Since urea and other nitrogenous matter form ammonia as one of their decomposition products, it occurred to us that this might be a source of contamination. A preliminary experiment was run to see if the presence of the animals would in any way effect our results.

Four bottles of the same size and shape of about one and one-half liters capacity were filled two-thirds full of ammonia free distilled water and exposed at various places.

No. 1 was corked at once to serve as a control on the original water.

No. 2 was exposed in the room where the ammonia distillations were to be carried out.

No. 3 was exposed in a room which was about three times as far from the dogs as was No. 2 and less liable to contamination.

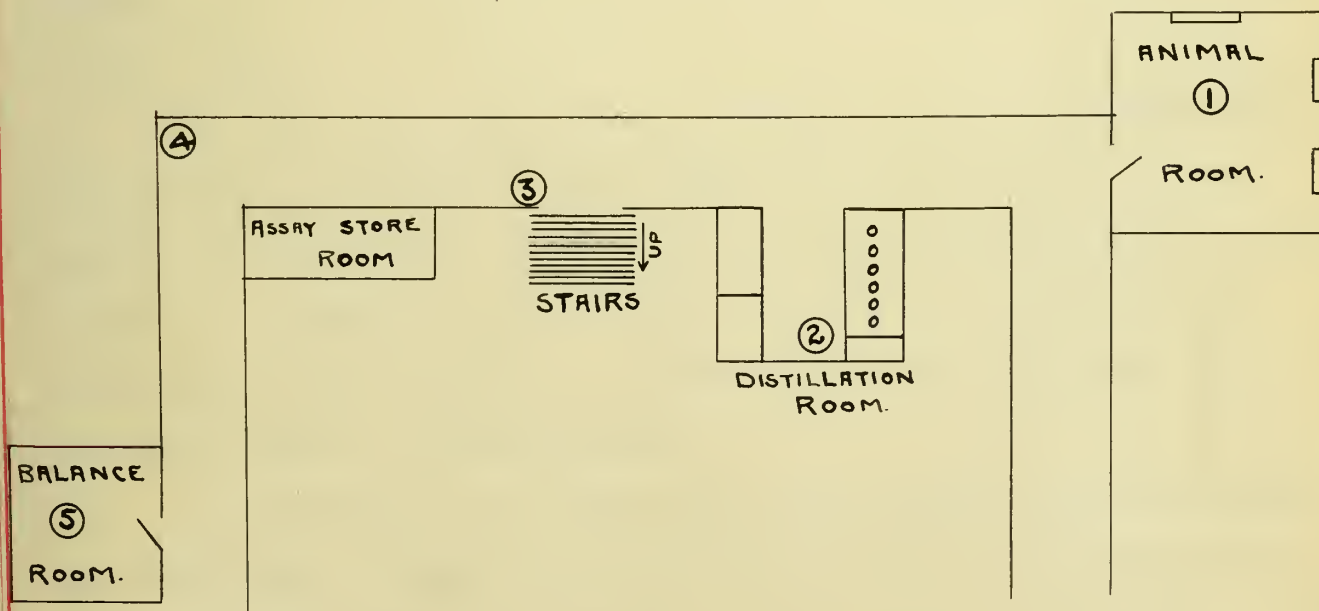
No. 4 was exposed in the room in which the dogs were kept.

Results in Parts per Million of Nitrogen

	No. 1	No. 2	No. 3	No. 4
NH ₃ found	.016	.052	.024	.582
Correction		<u>.016</u>	<u>.016</u>	<u>.016</u>
N from Dogs		.036	.008	.566

After the room had been thoroughly cleaned and aired, and with the wind blowing from the opposite direction, that is, away from the distillation room instead of towards it, another set of bottles containing distilled water was exposed and left for twenty four hours. These bottles six in number, were strung out down a long hall which opened directly into the room in which the dogs were, the bottles being about 60 feet apart. In this case as in the former the door was tightly closed and locked, and was only opened to care for the animals.

The diagram shows the position of the different bottles, as they were exposed with the exception of No. 6 which was corked at once and served as the control on the original water.



Results in Parts per Million of Nitrogen

No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
.102	.028	.020	.018	.018	.018
<u>.018</u>	<u>.018</u>	<u>.018</u>	<u>.018</u>	<u>.018</u>	<u>.018</u> correction
.084	.010	.002	.000	.000	.000 contamination from dogs.

It is noticable that the results here are very much lower than in the first experiment, the water put into the dog room showing .084 parts of nitrogen against .566 parts in the former case. This reduction in the amount of ammonia was doubtless due to the better conditions existing in the room in which the animals were kept. It is noticable that they still have an effect on the ammonia distillation. Another experiment under about the same conditions gave similar results and the dogs were moved soon after to another part of the building.

Since some authorities recommend the use of sodium carbonate in the distillation of free ammonia and some do not, it was desired to know whether the presence of the sodium carbonate had any effect on the amount of free ammonia obtained. All through the experiment a large variety of samples were run in one case with, the other without sodium carbonate.

The table on the next page shows clearly that the sodium carbonate does not lower or raise the results of the free ammonia. It is noticable that the results using sodium carbonate are a trifle higher, but the sodium carbonate by test showed from .001 to .002 parts of nitrogen present in the amount used, for which no correction was made. The addition of sodium carbonate increases the

EFFECT OF SODIUM CARBONATE ADDITION ON FREE AMMONIA.

Results in Parts per Million of Nitrogen.

Without Na ₂ CO ₃	With Na ₂ CO ₃
.064	.064
.072	.076
.016	.020
.136	.136
.018	.022
.066	.066
.060	.066
.064	.066
.082	.082
.078	.082
.016	.018
.022	.024
.094	.090
.064	.064

tendency of the solution to foam and boil over and hence should not be added except when the water to be examined has an acid, or very slightly alkaline reaction.

The ammonia content of the University water supply is very high yielding about 3.45 parts per million of nitrogen as free ammonia and 1.60 parts as albuminoid ammonia. This makes it extremely hard to obtain a water entirely free from ammonia. Ammonia free water which had gone through two distillations was used in all the experiments, and a test was run on it for every distillation. The chemicals and solutions used were tested in every case and all solutions were prepared as recommended by the Committee of the American Public Health Association on "Standard Methods of Water Analysis".

EXPERIMENTAL WORK.

Having eliminated the possible sources of error, and having found that it was more satisfactory to test the reagents and make a correction rather than to try to prepare them entirely free from ammonia, the effect on the ammonia determination of several salts which occur naturally in water was tried.

Effect of Calcium Acid Carbonate.-- The effect of calcium which is usually present as calcium acid carbonate was the first tried. An artificial water was made up containing 280 parts per million of calcium carbonate, by making a saturated solution of calcium hydroxide, and then passing carbon dioxide into the solution converting the hydroxide into the acid carbonate. The solution was then diluted with ammonia free water to give the desired

concentration of calcium acid carbonate. Six samples were distilled.

Nos. 1 and 2 contained 500 c.c. of ammonia free water and .06 parts of nitrogen which was added as ammonium chloride.

Nos. 3 and 4 contained 500 c.c. of calcium carbonate water and .06 parts of nitrogen which was added as ammonium chloride.

Nos. 5 and 6 consisted of 500 c.c. of carbonate water alone.

Since 5 and 6 contain the carbonate water alone, 3 and 4 minus 5 and 6 should equal 1 and 2.

Results in Parts per Million of Nitrogen

No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
.062	.060	.072	.076	.014	.018
----	----	.016	.016	----	---- correction
.062	.060	.056	.060	----	---- corrected

A duplicate of the above experiment was run using .12 instead of .06 of nitrogen.

Results in Parts per Million of Nitrogen

No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
.120	.120	.136	.136	.018	.022
----	----	.020	.020	----	---- correction
.120	.120	.116	.116	----	---- corrected value

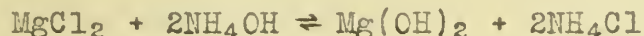
It is evident from the two sets of results above that calcium acid carbonate does not interfere with the determination of ammonia.

Effect of Magnesium.-- Kober* has shown that in the

presence of magnesium chloride all the ammonia is not given off. He

*J. Am. Chem. Soc. 30, 1279 - 81.

illustrated this by adding one cubic centimeter of a N/10 solution of ammonium chloride to a saturated solution of magnesium chloride and after adding three drops of a saturated solution of caustic soda and distilling, he was not able at any time to detect ammonia in the distillate. He explained this result on the reversibility of the reaction between magnesium chloride and ammonia.



According to the principles of physical chemistry we should not expect to find any ammonia in the distillate under these conditions. The high concentration of the magnesium chloride would drive the reaction to the right and if any ammonia should be formed it would immediately be acted upon by the magnesium chloride which is present in relatively large excess forming magnesium hydroxide and hence could not be detected in the distillate.

About ten per cent of the municipal water supplies of Illinois contain magnesium chloride, and the problem to be solved was to see if the concentration of the magnesium chloride in potable waters was large enough to have any restraining effect on the ammonia distillation. The average amount of magnesium chloride in water supplies of Illinois towns is 26.8 parts per million, the highest being 75 parts. Two different tests were run, one using 100 parts per million and the other 200 parts of magnesium chloride. In both cases .080 parts of nitrogen as ammonium chloride was added.

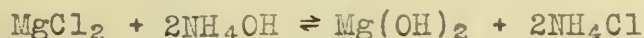
Results in Parts per Million of Nitrogen
200 Parts per Million of Magnesium Chlorides

.092	.094	----	----	----	----	Nitrogen obtained
<u>.014</u>	<u>.014</u>					Correction
.076	.080	N found		.080 N calculated		

100 Parts per Million of Magnesium chloride

.086	Nitrogen obtained		.086
<u>.012</u>	Correction		<u>.012</u>
.074	Nitrogen corrected		.074 Calculated .080

From the foregoing experiments it is evident that the concentration of magnesium chloride existing in water does not interfere materially with the determination of nitrogen as free and albuminoid ammonia. On first thought the variation between the amount of ammonia added and the amount found in the second test, suggests interference, but the variation in this case is far within the experimental error due to the rate of distillation, etc. and hence cannot be considered as any interference on the part of the magnesium chloride. Going back to the original equation



our results showing no interference with magnesium chloride can be easily explained. The concentration of the magnesium chloride is so low that the reaction does take place to some extent to the left. As the ammonia is formed it is volatilized and distilled off and more ammonia is formed until the reaction has gone to completion.

Effect of Hydrogen Sulphide.-- It has been suspected that the presence of hydrogen sulphide in a water might interfere with the determination of nitrogen as ammonia. In 1909 an analysis was made by several authorities of a sample of water for the purpose of agreeing on a standard method to be followed in making a mineral analysis of a water. The water contained hydrogen sulphide and one analyst expressed the opinion that ammonia could not be determined in the presence of the hydrogen sulphide. The effect of hydrogen sulphide was therefore studied in this work.

An artificial water was made up by taking ammonia free water and passing into it hydrogen sulphide which had been passed through hydrochloric acid to remove any traces of ammonia and then through water to remove any hydrochloric acid vapors. The hydrogen sulphide was bubbled through until the water showed a concentration of 56 parts per million. Three portions of 500 c.c. were taken and .06 parts of nitrogen as ammonium chloride added and the nitrogen determined in the usual way.

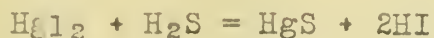
Results in Parts per Million of Nitrogen

Nitrogen found			Nitrogen taken
.082	.214	.376	.06

These results show wide variations among themselves and from the amount of nitrogen taken. In the third case the amount of nitrogen found was apparently six times the amount taken. It is hardly correct to make this statement either because the tubes had a yellowish cloudy color and not the true Nessler tint and the readings recorded were those of the standards which showed the

closest comparison.

Four more portions of water were taken and .06 parts of ammonia nitrogen added and the distillations made. In three of the four cases on nesslerization the first tube gave a black precipitate, evidently mercuric sulphide and it was impossible even to approximate



the reading. In the fourth case all four of the tubes gave a yellow color in which the reading could only be approximated being .262 when it should have been .06. It was very evident that nitrogen could not be determined in waters containing hydrogen sulphide, by distilling in the ordinary way.

Methods of Getting Rid of Hydrogen Sulphide.-- That hydrogen sulphide is present in a great number of mineral waters, and at times in very large amounts can be seen from the table on the following page. The data for this table was taken from Vol. 5 Bulletin No. 32 of the United States Geological Survey Report, and is entitled "Mineral Springs of the United States" by A. C. Peale, M. D.

The question resolved itself in how to get rid of hydrogen sulphide without losing any ammonia. There were two general methods of accomplishing this. One was to hold the sulphur in the flask while the ammonia was distilled off, by adding sodium hydroxide or lead acetate forming sodium sulphide or lead sulphide which would remain behind; the other method was to hold the ammonia in the flask and distil off the hydrogen sulphide. Both of these methods were tried, but the latter with the greater success.

MINERAL SPRINGS CONTAINING HYDROGEN SULPHIDE.

New York	Cu. in. per Imp. gal.	Parts per Million
Avon Sulphur Springs		
Upper Spring	12.00	60.0
Sawer Spring	10.02	50.1
New Bath Spring	31.28	156.4
Congress Hall Spring	27.63	138.2
Chittenango Springs		
White Sulphur Spring	.88	4.4
Cave Spring	2.75	13.8
Magnesia Spring	5.62	28.1
Columbia White Sulphur Spring	4.49	22.5
Doxtatters, Rochester,	17.28	86.4
Florida Spring	3.76	18.9
Lockport Mineral Spring	2.86	14.3
Sharon Springs		
White Sulphur Spring	20.50	102.5
Magnesia Spring	3.30	16.5
Red Sulphur Spring	10.50	52.5
Gardner Magnesia Spring	6.00	30.0
Richfield Springs		
St. Regis Spring	5.30	26.5
Unknown Spring	24.24	121.2
Sulphur Spring	3.62	18.1
White Sulphur Spring	14.20	71.0

Cu. in. per
Imp. gal,
.31

Parts per
Million
1.6

Magnesia Spring

Virginia

Buffalo Lithia Springs

Spring No. 1	5.9	24.5
Spring No. 2	8.3	41.5
Spring No. 3	3.4	17.0

Augusta Springs

Sulphur Spring No. 1	.91	4.6
Sulphur Spring No. 2	.24	1.2

Alabama

Cullem Springs

Sulphur Spring	97.10	485.5
----------------	-------	-------

Blount Mineral Springs

Red Spring No. 1	14.96	74.8
------------------	-------	------

Talladega Spring

82.00	410.0
-------	-------

Tennessee

Cascade Springs

23.04	117.2
-------	-------

Crisp Spring	9.47	47.4
--------------	------	------

Fernvale Spring	14.64	73.2
-----------------	-------	------

Hurricane Spring	1.16	5.8
------------------	------	-----

Jones Sulphur Well	1.17	5.9
--------------------	------	-----

Red Boiling Spring	4.50	22.5
--------------------	------	------

White Creek Spring	40.25	201.3
--------------------	-------	-------

	Cu. in. per Imp. gal.	Parts per Million
West Nashville Sulphur Well	5.84	29.2

Michigan

Mount Clemens Mineral Springs

Mount Clemens Mineral Well	34.77	173.9
Medea Spring	40.00	200.0
Soobad Spring	33.00	165.0

Ypsilanti Mineral Springs

Ypsilanti Well	21.08	105.4
Moorman Well	32.21	161.1
Owen Mineral Well	15.52	77.6
Wyandotte White Sulphur Spring	20.00	100.0

In the Kjeldahl method of determining nitrogen, the organic matter is digested with concentrated sulphuric acid and the ammonia which is formed combines as ammonium sulphate. Hydrogen sulphide is easily driven out of an acid solution. Therefore it seemed that by acidifying a hydrogen sulphide water with sulphuric acid and distilling off fifty or a hundred cubic centimeters of the solution that the hydrogen sulphide could be completely removed without affecting the ammonia.

In order to test this supposition an artificial water containing twenty parts per million of hydrogen sulphide was prepared. Normal solutions of sulphuric acid and sodium hydroxide were also made up. Four portions of 500 c.c. each of the artificial water were taken and .06 grams of nitrogen as ammonium chloride added. To each flask fifty cubic centimeters of normal sulphuric acid was added, making the solutions strongly acid. One hundred cubic centimeters of water were then distilled over. The first tube of 50 c.c. was cloudy and smelled very strongly of H_2S , and on the surface small flakes of free sulphur were visible, showing that the hydrogen sulphide was being driven off. The second tube or second 50 c.c. was fairly clear. After the 100 c.c. had been distilled over fifty cubic centimeters of normal sodium hydroxide was added which left the water slightly alkaline. Two hundred cubic centimeters of solution were now carefully collected and nesslerized.

Blank tests, Nos. 5 and 6, were run on the ammonia free water with .06 parts of nitrogen as ammonium chloride added.

Results in Parts per Million of Nitrogen.

Hydrogen Sulphide Water + .06 Parts of Nitrogen.				Ammonia Free Water + .06 Parts of Nitrogen	
.082	.080	.078	.082	.064	.066

It is noticable that while only .060 parts of nitrogen was added about .080 parts of nitrogen was found, but it is also noticable that the amount of ammonia found in all four cases was practically constant. All the tubes were clear and gave the true nessler color. The conclusion was drawn that the difference between the amount of nitrogen found and the amount added was due to ammonia present in the chemicals and to ammonia added in the preparation of the hydrogen sulphide water. It was again evident that in spite of all precautions everything must be tested and the proper corrections made.

A new artificial water was made up using extra precautions against contamination and a new series run.

A. Ammonia free water with .060 parts of nitrogen added was run. The ammonia free water alone was tested.

B. Hydrogen sulphide water with .060 parts of nitrogen added was run according to the method given before. The same determination was made leaving out the .060 parts of nitrogen.

From this it is seen that if the second determination in both A and B is subtracted from the first, the results of A should equal B and both should be .060 parts of nitrogen.

Results in Parts per Million of Nitrogen

H ₂ S - H ₂ O + .060N			H ₂ S Control		H ₂ O + .060N	H ₂ O Control
.082	.086	.082	.026	.028	.070	.014
.026	.026	.026	----	----	.014	Correction
.056	.060	.056	----	----	.056	Nitrogen found

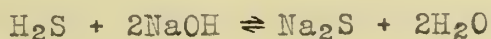
The whole experiment was duplicated only using a higher concentration of ammonia and of hydrogen sulphide. In this case the concentration of ammonia was .400 parts of nitrogen and the hydrogen sulphide 182 parts per million.

Results in Parts per Million of Nitrogen

H ₂ S - H ₂ O + .400N		H ₂ S Control	H ₂ O + .400N		
.416	.400	.030	.384	.352	
.030	.030	----	----	----	Correction
.386	.370	----	.384	.352	Nitrogen obtained

It is seen from the above results that nearly the correct amount of ammonia was found in a water containing hydrogen sulphide.

As stated before another method of determining the ammonia would be to hold the hydrogen sulphide in the flask either as sodium or lead sulphide while the ammonia was distilled off as usual. Sodium sulphide can be prepared by passing hydrogen sulphide into a solution of sodium hydroxide, but on the other hand solid sodium sulphide when dissolved in water hydrolyzes giving off some hydrogen sulphide. Our reaction then is a reversible one.



According to principles of physical chemistry the reaction can be forced to completion by making the concentration of the hydrogen sulphide, or the sodium hydroxide very large in comparison to the

remaining one. Since the hydrogen sulphide was the constituent we wished to get rid of an excess of sodium hydroxide was added to the hydrogen sulphide waters and the determination of ammonia made as usual. The result, however, was not satisfactory as some hydrogen sulphide still distilled over with the ammonia causing a cloudy precipitate in the tubes. It appears, therefore, that the concentration of sodium hydrate that would be necessary to hold the hydrogen sulphide is too great for practical purposes.

Phelps* in his work on the direct nesslerization of sewage

*Journal of Infectious Diseases. 1904, Vol. I. p. 327

made mention of the fact that if hydrogen sulphide is present in sewage, it should be precipitated with lead or zinc acetate. The fact suggested itself that the hydrogen sulphide might thus be precipitated as the sulphide in the distillation method for potable waters, so a comparison of this method was made with that of the sulphuric acid method.

The water used in this test contained 66 parts of hydrogen sulphide and .06 parts of nitrogen. Four portions of the hydrogen sulphide water were taken and 50 c.c. of normal sulphuric acid added to each. Two of these were neutralized at once with 50 c.c. of normal sodium hydroxide and 2.5 grams of lead acetate added, and the ammonia distilled. One-hundred cubic centimeters were distilled off of the other two as usual, the sodium hydroxide added, and the two hundred cubic centimeters for the ammonia determination collected. A control was also run on the water and chemicals.

COMPARISON OF SULPHURIC ACID AND LEAD ACETATE METHOD.

Results in Parts per Million of Nitrogen

Sulphuric Acid Method				Lead Acetate Method		
H ₂ S-H ₂ O + .060N		H ₂ S - H ₂ O Control		H ₂ S-H ₂ O + .060N		
.090	.088	.028	.030	.074	.056*	
.029	.029	----	----	.029	.029	Correction
.061	.059	----	----	.044	.027	Nitrogen obtained

*Yellow precipitate in second tube could not be read.

The results of the lead acetate method were low, indicating that the precipitate of lead sulphide held back some of the ammonia. One of the tubes gave a yellow precipitate with the nessler solution and could not be read, and in general the tubes were not as clear as the tubes obtained by the acid method.

A more extensive experiment was run in the same manner.

A.1. The sample of hydrogen sulphide water with .060 parts of nitrogen added was run according to the sulphuric acid method.

2. The hydrogen sulphide water and chemicals were run alone.

B.1. The sulphide water with .060 parts of nitrogen added was run by the lead acetate method.

2. The sulphide water and lead acetate were tested.

C.1. Ammonia free water plus .060 parts nitrogen was run.

2. The water alone was tested.

COMPARISON OF SULPHURIC ACID AND LEAD ACETATE METHOD.

Results in Parts per Million of Nitrogen.					
Sulphuric Acid Method		Lead Acetate Method		Check	
.094	.090	.026	.072	.074	.074 1st reading
.034	.034	.022	.024	.016	.018 Correction
.034		.023		.017 Mean Correction	
.060	.056	.003*	.049	.057	.057 Nitrogen Found

*No Na_2CO_3 . Solution probably not alkaline enough to give up its ammonia.

Having shown that the sulphuric acid method gives more reliable results than the sulphide method, one important question remained to be solved. Does the sulphuric acid added have any effect on the amount of free or albuminoid ammonia obtained?

In the determination of total organic nitrogen, as pointed out before, the water is boiled down and digested with concentrated sulphuric acid, and the amount of ammonia obtained is on the average about one-third greater than the sum of the free and albuminoid ammonia. Since in the sulphuric acid method fifty cubic centimeters of normal sulphuric acid are added there remained the possibility that more of the nitrogenous substances might be broken up so that the amount of ammonia obtained by this method would be larger than that obtained by the ordinary method.

To test this question a series of waters were run by both methods. The waters employed being nine waters sent in from different parts of Illinois for analysis by the State Water Survey and may be taken as typical of the waters of this State.

The results while they are not in all cases identical by

both methods show that the sulphuric acid has no effect on the amount of ammonia obtained; first because the variation between the two methods are first on one side then on the other and secondly because the variation is far within the experimental error.

THE EFFECT OF ADDING SULPHURIC ACID ON THE AMOUNT OF AMMONIA OBTAINED.

Serial No.	Free Ammonia			Albuminoid Ammonia			Total Ammonia		
	Ordinary Method	Sulphuric Acid Method	Average	Ordinary Method	Sulphuric Acid Method	Average	Ordinary Method	Sulphuric Acid Method	Average
20993	.010	.040	.028	.088	.096	.092	.104	.136	.120
21004	.024	.032	.028	.072	.056	.064	.096	.088	.092
21005	.048	.056	.052	.112	.096	.104	.160	.152	.156
21006	.024	.024	.024	.064	.056	.060	.088	.080	.184
21007	.120	.144	.132	.432	.432	.432	.552	.576	.569
21008	.080	.088	.084	.144	.128	.136	.224	.216	.220
21086	.544	.544	.544	.288	.288	.288	.832	.832	.832
21087	.864	.864	.864	.160	.152	.156	1.024	1.016	1.020
21088	.144	.152	.148	.104	.096	.100	.248	.248	.248

CONCLUSIONS.

1. The addition or omission of sodium carbonate before the distillation of free ammonia has no effect on the amount of ammonia found if the water is originally alkaline. If the water is acid sodium carbonate must be added before distillation. The addition of sodium carbonate does increase foaming and hence should not be added unless necessary.

2. Calcium acid carbonate or calcium salts in the quantities present in potable waters does not interfere with the determination of nitrogen as ammonia.

3. Magnesium chloride in the quantities found in potable waters does not hinder the determination of ammonia.

4. Ammonia nitrogen cannot be determined in the usual manner in a water containing hydrogen sulphide.

5. Ammonia nitrogen can be determined in the presence of hydrogen sulphide according to the following method:

To 500 cubic centimeters of the water to be examined add fifty cubic centimeters of normal sulphuric acid and distil off one hundred cubic centimeters of solution. Add fifty cubic centimeters of normal sodium hydroxide and collect two hundred cubic centimeters of solution for the determination of free ammonia. Albuminoid ammonia is determined as usual.

1. The addition of the sulphuric acid has no effect on the amount of free or albuminoid ammonia obtained.

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